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Description

Retroreflective sheeting has particular use in making highway signs, street signs and the like, and is now employed extensively. The Federal government has recognized two primary types of retroreflective sheeting: glass bead and cube-corner. Such approved sheeting materials are found in a specification entitled "FP-79", published by the U.S. Department of Transportation, Federal Highway Administration. Specification FP-79 presently has been adopted as a purchasing standard by many state highway departments, and it sets forth certain minimum specifications which must be met by retroreflective sheeting of the cube-corner type. Included among the specified characteristics are those for reflectivity, color, flexibility of material and resistance to cracking and weathering.

Cube-corner type reflector elements generally provide a higher specific intensity at 0.2° observation angle and 0° entrance angle than do glass bead type reflector elements, but, to applicant's knowledge, no one successfully has furnished a sheeting material in commercial quantities which generally will meet the requirements for the Class IIIB sheeting set forth in the aforementioned FP-79 specification. It therefore is a primary object of the present invention to provide a unique sheeting product which will substantially meet such specified criteria and which can be produced in accordance with the novel methods disclosed herein in an economical fashion and in commercial quantities.

Retroreflectivity is achieved by cube-corner type reflector elements primarily through the principle of total internal reflection. It is well known that any surface contact made by another material with the faces of the cube-corner elements generally has a deleterious effect on the reflectiveness of the reflector element.

However, when all of the element faces are metallized, or mirrored, then, rather than relying upon total internal reflection, retroreflection is achieved by specular reflection from the mirrored faces. Generally, metallizing will provide a grayish or black coloration under certain daylight conditions vis-a-vis unmetallized cube-corner type elements.

The present invention relates generally to methods and apparatus for producing retroreflective sheeting constructions and, more particularly, to methods and apparatus for producing a flexible laminate sheeting construction including an upper thermoplastic sheet, the reverse of which is provided with a repeating, retroreflecting pattern of fine or precise detail, a backcoating to protect the formed pattern, and a selectively applied intermediate layer allowing bonding of the backcoating to overlay the formed pattern on the thermoplastic sheet while preserving and enhancing the retroreflective properties of both the formed pattern and the laminated sheet. More precisely, the present invention is applicable to the production of cube-corner type retroreflective sheeting laminates.

Within the art of designing reflectors and retroreflective material, the terms "cube-corner" or "triangular," or "tetrahedral" are recognized in the art as describing structure or patterns consisting of three mutually perpendicular faces, not limited to any particular size or shape of the faces, or the orientation of the optical axis of the cube-corner element. Each of the cube-corner faces can assume a different size and shape relative to the others, depending upon the angular reflective response characteristics desired, and the cube forming techniques employed.

Examples of prior cube-corner type reflectors may be found in U.S. Patent No. 1,906,655, issued to *Stimson*, and U.S. Patent No. 4,073,568, issued to *Heasley*. *Stimson* shows a reflex light reflector including an obverse face and a reverse light-reflecting face consisting of a plurality of cube-corner type reflector elements with each such element having three mutually perpendicular surfaces adapted for total internal reflection of light impinging thereon from the obverse face. *Heasley* describes a cube-corner type reflector in the form of a rectangular parallelepiped.

It long has been desired to obtain the benefits of cube-corner reflective properties in the form of flexible sheeting. As noted above, one advantageous aspect of such sheeting is in the manufacture of highway and street signs, markers and the like, where graphics are printed, painted, silk-screened or otherwise applied to a highly reflective substrate mounted to a flat, stiff, supportive surface. Flexible retroreflective sheeting, when used as such a substrate, can be stored and shipped while wound onto rolls, and can readily be cut or otherwise formed into the desired shape and size required for a particular application. The reflective nature of the sheeting allows such signs, markers, and the like to reflect light from a vehicle's headlights, permitting the item to be read by the driver, without requiring a permanent light source to illuminate the sign or marker.

Production of such retroreflective sheeting has been made practicable by apparatus and methods to form precise cube-corner patterns in greatly reduced sizes on flexible thermoplastic sheeting. Desirably, such sheeting may then be assembled in the form of self-adhesive laminates.

Others have recognized the desirability of producing retroreflective thermoplastic material in sheet form. United States Patents Nos. 2,310,790, 2,380,447, and 2,481,757, granted to *Jungersen*, describe and teach the shortcomings of previously-known reflectors manufactured from glass, and the advantages inherent in providing a reflective material in a less fragile and more flexible sheet form. While so suggesting, it is not known if *Jungersen* in fact ever commercialized any product disclosed in such patents.

In U.S. Patents Nos. 4,244,683 and 4,332,847 issued to *Rowland*, the desirability of manufacturing cube-corner retroreflective sheeting in a continuous, non-stop process is presented, but the approach selected by *Rowland* is a "semi-continuous" process (*Rowland* '683, column 2, lines 1838), presumably so-called because the process requires frequent repositioning of the molding plates.

In United States Patent No. 3,187,068, issued to *DeVries, et al.*, continuous production of reflective sheeting is disclosed, utilizing encapsulated glass microspheres as the reflecting medium. *DeVries, et al.* describes the application of a pressure-activated adhesive layer to such sheeting to enable attachment of sheeting segments to selected surfaces.

In United States Patent No. 3,649,352, issued to *Courneya*, a beaded sheeting construction is described, portions of which become reflective when heated, and which includes a pressure-activated adhesive layer allowing attachment of the sheeting construction to other articles.

Palmquist, et al., 2,407,680 teach the utilization of glass microspheres or beads included as the reflective elements in flexible sheet forms; *Tung, et al.*, in United States Patent No. 4,367,920, also describes a laminated sheet construction using glass microspheres as the reflective elements.

A common problem in the construction of reflective laminate sheeting is to find means to bond the lamina firmly together in a way which preserves the required retroreflective qualities of the reflective elements selected for use. An example of prior efforts to solve this problem with respect to glass microspheres may be seen in United States Patent No. 3,190,178, issued to *McKenzie*, wherein a cover sheet or film is secured over exposed glass microspheres by use of die elements which force a portion of the material in which the glass microspheres are embedded into contact with the cover sheet. The die elements thus create a grid pattern on the resulting sheeting construction, with each grid forming a separate cell. Within each cell, an air space is maintained between the microspheres and the cover sheet, and incident light traverses the cover sheet and the air space to be retroreflected by the embedded microspheres.

Holmen, et al., U.S. Patent No. 3,924,929, teach a cube-corner type upper rigid sheet having upstanding walls, or septa, integrally formed as part of the cube pattern. The septa extend to form a regular geometric pattern of individual cells, with the septa extending at least as far from the upper sheet as the cube-corner elements. A particulate packing may be used to fill each of the cells, and a backing sheet is then attached to the rear of the upper sheet, with the septa serving as the attachment sites. *Holmen, et al.* use relatively large cube-corner elements fashioned as rigid sections bound to a flexible back, and has limited flexibility in use.

In *McGrath*, U.S. Patent No. 4,025,159, the cellular concept is described with respect to cube-corner type retroreflective sheeting, through use of dies to force a carrier film into contact with the reverse side of the cube-corner sheeting. The carrier film must then be cured with radiation to bind it to the cube-corner sheeting and, as in *McKenzie*, the resulting cells include an airspace extending between the carrier film and the reverse side of the cube-corner sheet. The air cell structure apparently was intended to provide a hermetically sealed cell, avoiding the need for metalizing the cube-corner elements, and providing an air/thermoplastic interface to enhance retroreflection.

None of the foregoing teach the assembly of molded or embossed cube-corner type retroreflective sheeting into self-adhesive laminates which protect and enhance the reflective properties of the sheeting without requiring the use of dies or of integrally-molded septa or walls included as part of the cube pattern. Further, none of the foregoing permits the material to benefit from encapsulated sections of cube-corner elements while enhancing and substantially meeting the requirements specified in the aforementioned DOT FP-79 Specification.

The present invention is an improvement over the invention disclosed in our application EP—A—0 142 250, which forms part of the state of the art by virtue of EPC Article 54(3) only. That application discloses a relatively flexible retroreflective laminate sheet construction including a thermoplastic web with a light-receiving and transmitting front side and a reverse side coextensive with the front side, a retroreflective pattern being formed on the reverse side. A layer is deposited on the reverse side to cover selected portions of the formed retroreflective pattern with the remaining portions of the formed pattern devoid of the granular material. A layer of back coating material is deposited on the reverse side to overlay the granular material. The back coating material contacts the remaining portions of the formed pattern and is fixedly secured thereto, thereby encapsulating the granular material between the reverse side and the back coating layer.

The present invention provides a method of producing a cube corner type retroreflective laminate sheet construction, the method comprising the steps of: (a) applying to a web of thermoplastic material having a retroreflective cube corner formed pattern devoid of septa on at least a portion of one side, a layer of hydrophobic granular material deposited so as to form a regular and repeating array on the retroreflective pattern; (b) forming, as part of the said array, a plurality of paths on the said one side devoid of the hydrophobic granular material; (c) applying a layer of backcoating material to overlay the hydrophobic granular material and to fill the said path, the particle size of the hydrophobic granular material being such that the area in which it is deposited is substantially impervious to the backcoating material so that the backcoating material is unable to penetrate the granular material and come into immediate contact with the said one side except in the area devoid of the granular material; (d) adhering the backcoating material to encapsulate the hydrophobic granular material between the said one side and the backcoating material; and (e) securing an overlayer of weather-resistant thermoplastic material, containing absorbers or reflectors of radiation in about the ultra-violet range, to that side of the said web opposite to the side on which the cube corner pattern is formed.

The invention also provides a flexible retroreflective cube corner type laminate sheet construction produced by the said method including a thermoplastic web with a light-receiving and transmitting first

side and a second side coextensive with the first side, and a cube corner type retroreflective pattern devoid of septa formed on at least a portion of the second side, a layer of hydrophobic granular material covering selected portions of the cube corner retroreflective pattern with remaining portions of the second side devoid of the hydrophobic granular material; a layer of backcoating material substantially completely
 5 overlaying the hydrophobic granular material and substantially fully contacting the said portions of the second side devoid of the granular material and being fixedly secured thereto, thereby encapsulating the hydrophobic granular material between the second side and the backcoating layer without penetrating the granular material and coming into immediate contact with the second side except in the area devoid of the granular material; and a lamina of flexible thermoplastic material co-extensive with and secured to the
 10 light-receiving and transmitting first side of the thermoplastic web, the said lamina including means for inhibiting radiation in about the ultraviolet range.

A preferred process will now be described.

A thermoplastic sheet or web is provided on its reverse side with a retroreflective cube-corner type pattern devoid of septa. A thin layer of a liquid vehicle or solvent containing hydrophobic granular material
 15 (such as silica treated with silanes) is deposited on the reverse side of the web, as by screen printing, in a pattern leaving selected sites devoid of granular material. The web is then dried to drive off the solvent and, thereafter, a water-based backcoating is applied over the granular material pattern, with portions of the backcoating being in direct contact with the thermoplastic web at those sites on the web devoid of granular material. Thereafter, the backcoating is dried or cured, and a layer of adhesive such as pressure-sensitive or
 20 heat-activated adhesive is applied thereto. The procedure thus enables the assembly of patterned web material into laminates which include an activated adhesive layer while protecting the retroreflective properties of the precisely formed cube-corner pattern.

A thin layer of a hydrophobic silica mixture is then screened or sprayed onto the embossed reverse surface of the laminated thermoplastic web in a diamond-like pattern, and is thereafter dried. A
 25 water-based backcoating mixture of certain formulation is next deposited over the silica layer to encapsulate the silica and to contact the thermoplastic sheet where no silica was deposited. The backcoating then is heat dried and/or cured to form a continuous film. A pressure-sensitive or heat-activated adhesive then is applied to the cured backcoating layer, with the adhesive protected by a release sheet which is removed when the laminate is applied to an object.

An outer protective layer of thermoplastic material inhibiting ultraviolet radiation, used to provide additional weather resistant properties, is secured to the thermoplastic web on the side opposite from that upon which the retroreflective pattern is formed during or before the cube forming process.

The completed laminate is then cut, trimmed, or otherwise shaped for application to supporting surfaces, such as street or highway signs, and graphics or other indicia may thereafter be painted, printed,
 35 silk-screened, or otherwise affixed to the uppermost surface of the laminate, thus producing a readily and easily constructed highly retroreflective finished product.

These and further aspects of the present invention will become more apparent upon consideration of the accompanying drawings, wherein:

Fig. 1 is an enlarged perspective and somewhat schematic view of one preferred aspect of the retroreflective sheeting before the application of a weather-resistant overlayer;

Fig. 2 is a view along line 2—2 of Fig. 1;

Fig. 3 is a greatly enlarged plan view illustrating a section of the formed surface of the reflective sheeting;

Fig. 4 is a somewhat schematic and symbolic view of the processes and machinery utilized in a preferred aspect of the present invention;

Fig. 5 is a plan view of one form of screen pattern used to apply the hydrophobic granular layer;

Fig. 6 is an enlarged view, in partial detail, of an individual cell of the sheeting; and

Fig. 7 is an enlarged perspective view of a complete embodiment of the retroreflective sheeting of the present invention.

Referring now to Fig. 3, the numeral 10 indicates generally a segment of cube-corner type retroreflective thermoplastic web used in forming the laminate of the present invention. As seen in Fig. 3, there is depicted the rear surface of a portion of flexible retroreflective sheeting 12 fashioned from transparent thermoplastic material in web form which has formed thereon, preferably by embossing, a retroreflective and repeating pattern of cube-corner reflector elements characterised by cube faces 14, 16,
 55 and 18 and being devoid of septa. In a preferred aspect of such sheeting, sheet 12 is formed from an impact-modified acrylic material having UV inhibitors or absorbers added thereto, and which, prior to embossing, had parallel front and back surfaces and was initially on the order of about 0.15 mm (0.006 inch) thick. One such material is known as Plexiglass DR, sold by the Rohm and Haas Company.

The cube-corner pattern formed on sheeting 12 is formed in an optically precise, finely-detailed pattern. For example, as seen in Fig. 2, the depth to which the cube-corner pattern is embossed onto sheet 12 may be of the order of 0.0859 mm (0.00338 inch) (dimension X). As shown at dimension Y in Fig. 3, the cubes formed on sheet 12 may be spaced apart by a distance on the order of about 0.18 mm (0.0072 inch), for the depth as shown at X as set forth above. While the cube pattern in Fig. 1 illustrates cubes formed with their optical axes normal to the face of sheet 12, it is to be understood that other versions and patterns may
 65 also be utilized as forming the retroreflective web of the laminate of the present invention.

Referring now to Fig. 1, the numeral 20 indicates generally a roll of retroreflective laminate 22 manufactured in accordance with preferred aspects of the present invention to be described hereinbelow, before application of the weather-resistant overlay. As herein shown, laminate 22 is rolled onto a core 24. A thermoplastic web 26 having a front or obverse surface 28 and a rear or reverse surface 30 upon which is embossed the cube-corner type retroreflective pattern is illustrated in Fig. 3. The thermoplastic web 26 may be on the order of about 0.15 mm in thickness (0.006 inch).

Bonded to the reverse surface 30 of the thermoplastic web 26 is backcoating or film 32. In a preferred aspect of the present invention, a hydrophobic granular silica material 34 is interposed between the backcoat film 32 and the reverse side 30 in a manner to be described hereinbelow.

In accordance with a preferred embodiment of the present invention, a layer of adhesive 36 is bonded to a release sheet 38 in a presently well-known fashion, and is thereafter bonded to cured backcoat film 32 in order to provide a finished laminate 22 which includes a pressure-sensitive or heat-activated adhesive layer 36 applied to sheeting 12 in a manner which preserves the retroreflective qualities and properties of the cube-corner pattern embossed thereon. The release sheet 38 is used to protect adhesive layer 36 until it is desired to apply laminate 22 to a given surface.

Fig. 4 shows, in schematic form, a preferred arrangement of equipment and sequence of operations to produce a retroreflective sheeting laminate of the type shown in Fig. 3.

The application of adhesive directly to the reverse side of a cube-corner embossed thermoplastic web 26 will cause an undesirable and unacceptable loss of retroreflective capability. This arises from the contact of the adhesive material with the obverse side of embossed thermoplastic web 26, *i.e.*, the filling of the "valleys" formed by the embossed pattern and the subsequent interface formed between substances that are too similar in refractive indices to produce adequate retroreflection, so the transparent film can no longer utilize the phenomenon of total internal reflection to efficiently effect retroreflection of light. To solve this problem a substantial portion of the cube-corner pattern either must be hermetically sealed with an air space between the back wall and the cube-corner elements, or the cube-corner elements must be backed in a way which would preserve the retroreflective properties of the formed web while providing sites for firm attachment of an adhesive layer (or other adhesive material). Without such protection, and without such attaching sites, the use of, and effectiveness of a retroreflective embossed web is seriously compromised and curtailed.

Unexpectedly, use of hydrophobic granular materials has been found to afford such protection of optical properties. Among such materials are xylenated glass particles, powdered silicone rubber, and silane-treated silica.

As part of the present invention, it has been found that a hydrophobic silica mixture consisting principally of amorphous silica treated with silanes, when used to fill the valleys formed by the embossed pattern, preserves the retroreflective properties of the formed pattern for most practical purposes. Again, it is not known precisely why this effect obtains; it has been theorized that the point contact of granules with the reverse face of the embossed thermoplastic web acts to preserve the retroreflective properties of the pattern, perhaps by preserving a sufficient air interface with the reverse side of the cube-corner pattern. However, the present invention obtains excellent results even where the primary silica particles used are significantly smaller than, for example, the particles discussed in prior art patents such as *Holmen, et al.*, U.S. Patent No. 3,924,929.

Use of such silica offers advantages such as low price, availability, and ease and precision of formulation. It further provides unique color and reflective characteristics to the film which improves the appearance of the film even relative to the glass bead types heretofore commonly used.

As discussed hereinabove with respect to the *Holmen, et al.*, reference, others have attempted to solve the problem of loss of reflectivity by providing upstanding walls or septa as part of the rigid molded front face pattern, with the septa forming individual pockets for the application of granular compounds having particle sizes far in excess of the silica particles used in the present invention. The disadvantages to such an approach, particularly with respect to the cube-corner type embossed pattern utilized in the present invention are manifest. Use of rigid septa limits the size and shape of the cell. A separate mold must be formed for each type of retroreflective sheeting requiring a cell size other than that formed in the original mold. What is meant by the term "cell size" is the area bounded by or closed off by the walls to form a single pocket for the granular backing material.

Formation of such septa in a relatively rigid mold pattern manufactured to as fine and precise a degree of detail as that shown in the present invention also may cause problems with respect to stripping the formed thermoplastic web from the forming tool. This may particularly be a problem where the septa or walls extend inwardly into the mold to a distance greater than the depth of the cube-corner pattern.

A preferred embodiment of the present invention includes the mixing of a hydrophobic silica mixture using hydrophobic silica, organic solvents, and thickeners, and the application of this mixture, while in a liquid form, to the reverse side of the formed thermoplastic web in a desired pattern. One advantage of the present process and product is that the pattern can conveniently be changed to effect changes in reflective capability of the film, without changing the tools used in forming the embossed web. Thereafter, the partially coated or imprinted thermoplastic web is passed through a drying oven which drives off the solvents used to form the mixture, thereby drying the pattern on the thermoplastic sheet. The pattern in which the silica is applied to the thermoplastic web leaves selected portions or sites on the formed face of

the thermoplastic web devoid of silica.

Referring now to Fig. 5, the numeral 40 indicates generally such a selected pattern. Each runner or path 42 represents an area on the reverse surface of thermoplastic web 26 where no silica has been deposited. Each square or diamond-shaped area 44 represents an area on the surface of thermoplastic web 26 onto which the silica mixture has been deposited.

As seen in Fig. 6, the actual percentage of area covered by the silica mixture is determined by the thickness or width of each runner or path 42, and the pattern selected for deposition of the silica, with the cell 44 having an area bounded by the runners 42, and fully available for the reception and retroreflection of incident light by the embossed retroreflective patterns shown partially at 46.

Referring now to Fig. 4, it may be seen that thermoplastic web 26 may be drawn directly from an associated forming machine (not herein specifically shown) in a continuous process, or may be drawn from a separate supply reel onto which the embossed web 26 has been wound (not herein specifically shown). If desired, web 26 may be supported by a backing sheet (not herein specifically shown) coextensive with obverse face 28, leaving reverse surface 30 exposed.

It should be noted that reference to web 26 also includes reference to a laminate formed by web 26 and a backing sheet such as described hereinabove.

Web 26 is drawn by, for example, powered rollers (not herein specifically shown), to silica mixture application station 48. As herein diagrammatically shown, a preferred means and method of applying the silica mixture to web 26 may be accomplished through use of a screen-printing cylinder 50 which has mounted about the outer periphery thereof, a metal screen formed to provide the shape or pattern to which it is desired to apply the silica mixture. The mixture is forced under pressure from the interior of screen-printing drum onto the reverse side 30 of the thermoplastic web 26. As herein shown, the web 26 is directed by idler roller 52 to pass between the screen-printing drum 50 and a backing roller 54.

A preferred form of the apparatus utilized to apply the silica mixture at application station 48 consists of a drum printer manufactured by Stork Brabant BV of Boxmeer, Holland, of the type having a drum with electro-formed mesh screens over which a photo-resist pattern (such as used for conventional silk screen) may be mounted, with a screen pattern providing a diamond cell size in the range of from about 2.44 mm (0.096 inch) to 7.62 mm (0.300 inch), and a runner or cell wall thickness of from about 0.25 mm (0.010 inch) to about 1.27 mm (0.050 inch). Variations in the shape of the cells, pattern repeat of the cells, and thickness of the runners may be accomplished by changing the printing screen used on screen-printing drum 50. Also, the constant width of the web may be of various sizes, and the printing screens used will be of a compatible width.

In its preferred form, the silica mixture is made from a hydrophobic silica such as that manufactured by the Pigments Division of Degussa, of Frankfurt, West Germany, under the trade designation Sipernat D10. A preferred composition of the mixture includes hydrophobic silica in a mixture containing approximately 98 percent silane-treated silicon dioxide (SiO_2); 0.8 percent sodium oxide (Na_2O), and 0.8 percent of sulfur trioxide (SO_3); a non-polar aliphatic hydrocarbon solvent carrier; a polar solvent; and, where desired or required, a thickening agent. One aliphatic non-polar hydrocarbon solvent successfully used is low odor mineral spirits, and a workable mixture has been created through use of an organic alcohol, preferably butanol, as the polar solvent material. A smectite clay-based thixotropic thickener also may be used in varying amounts to produce a well-defined screen-printed pattern of the silica slurry on the embossed thermoplastic web.

In its preferred embodiment, the primary particle size of the silica is about 18 nanometers, and the agglomerated particle size of the hydrophobic silica in its final form is about 5 μm . However, it will be understood that the only critical limitation on the particle size is such that the area in which it is deposited will be substantially impervious to the backcoating material 32, whereby the backcoating material is unable to penetrate the hydrophobic silica and interact with the cube-corner pattern except in those areas devoid of the silica.

The particular combination of solvents and thickeners is important to satisfactory deposition and definition of the silica in a precise and accurate pattern. Screen printing of particulate material commonly requires use of resins or other binders to hold the deposited particles in place. A resin or binder cannot however be used in this instance because of the adverse effect on reflectivity of the web because of refractive index similarities.

Another important consideration is the rheology, or flow characteristics of the silica slurry as it is forced through the printing screen. The slurry must "relax", or thin as it is forced through the screen apertures, and thereafter regain sufficient viscosity to retain a well-defined pattern with good leveling qualities and appearance characteristics. Yet another consideration is use of a solvent vehicle which obtains the aforementioned qualities without attacking or degrading the thermoplastic web upon which the retroreflective pattern is formed.

Use of polar solvents, such as butanol, enables the slurry to maintain an increased concentration of solids (silica). Such solvents, however, react with the thermoplastic material used to form the web. Non-polar solvents, such as mineral spirits, preserve the embossed web, yet do not act to provide a satisfactory silica pattern. Therefore a blend of polar and non-polar solvents has been found to be useful in carrying enough solids without degrading reflectivity or degrading the web.

Preferably, the hydrophobic silica is present in proportions ranging from about 15 percent to about 35

percent by weight, the non-polar solvent carrier is present in amounts ranging from about 40 percent to about 70 percent, the polar solvent is present in amounts ranging from about 10 percent to about 30 percent, and the thickening agent may be present in amounts from about 2 percent to about 8 percent. One preferred formulation of the silica mixture includes 20 percent by weight Sipernat DIO hydrophobic silica,
 5 56 percent mineral spirits, 20 percent butanol, and 4 percent thickener. It has been found that such proportions preserve the web while providing a useful silica pattern.

After application of the silica mixture, web 26 is passed through a heating oven 56 where the resulting silica pattern is heated to drive off the organic solvents without heating web 26 to the point where heat distortion of the cube-corner elements of the laminate will occur.

10 After drying, the silica is mechanically held to the cube-corner elements on the reverse face 30 of web 26 by, it is believed, electrostatic forces and physical inter-engagement of the silica particles themselves.

Thus, as web 26 exits mixture application station 48, it has taken on the form of a first modified laminate 58, i.e., a web 26 having cube-corner elements with a precisely formed pattern of silica mixture screened thereon over a portion of the elements, with an uncovered portion of the cube-corner elements
 15 still exposed. As modified laminate 58 exits drying oven 56, it takes on a second modified laminate construction 60 wherein the solvents present in the silica mixture have been driven off and the silica itself has remained dried into its screened-on pattern.

The second modified laminate 60 then enters a backcoating application station 62. The application of a water-based backcoating accomplishes several results. First, those areas onto which no silica has been
 20 screened or deposited will allow direct contact between the backcoating and the reverse side 30 of the embossed or otherwise formed thermoplastic web 26, thus "wetting" web 26 with the liquid backcoating mixture. Second, a layer of backcoating material will overlay the silica pattern formed on thermoplastic web 26 and, when applied effectively, will not disturb or disrupt the printed or screened-on silica pattern. Third, the backcoating may then be dried and/or cured to provide a firm attachment to thermoplastic web
 25 26 to provide a flat, smooth and integral surface upon which further layers, such as a layer of pressure-sensitive or heat-activated adhesive may be effectively and conveniently applied, and to protectively cover or encapsulate the silica pattern. A surprising and unexpected result is that the silica prevents permeation by the liquid backcoating to the cube-corner pattern. As described above, such permeation would adversely affect the reflectivity of the final assembled laminate.

30 Application of the backcoating mixture to the second modified laminate 60 may be accomplished in a number of ways, such as by spraying, roller application, squeegeeing, or the like. The manner in which the backcoat is applied will be determined by, *inter alia*, the precise formulation of the backcoat and the pressure, or force, which can be withstood by the silica pattern after it has been dried.

For purposes of illustration, a backcoating application station 62 may be characterized as having a
 35 supply header or tank 64 communicating with an application means 66 which may be a nozzle or series of nozzles, or the like. An implement such as a doctor blade 68 may be used to more uniformly spread the backcoating after it has been applied without damaging the silica pattern. A platen 70 provides support for the second modified laminate 60 during application of the backcoat.

After application, the third modified laminate 72 enters drying oven 74 wherein the backcoat material is
 40 heat-cured, resulting in backcoating layer 32 as shown in Fig. 1.

Successful use of a backcoating requires that the backcoating formulation meet several particularly important working parameters. One is that the backcoating have flow characteristics such that the relatively narrow and shallow runners formed by the silica pattern will be filled, while not dewetting or disturbing the dried silica pattern itself. This means that the viscosity of the backcoating must be carefully controlled to
 45 assure that the backcoating can be applied while completely encapsulating without disturbing the silica pattern. Another characteristic is that the backcoating cannot penetrate or interact with the applied silica to reach the interface between the silica and the cube-corner pattern. Yet another requirement is that the backcoating, when dried, have the required flexibility and toughness to withstand use in a laminate. Ideally, the backcoating should also be of a color which enhances daytime visibility of articles made with such
 50 laminates.

Several preferred backcoatings have been utilized. Each may be characterized generally as including a water-borne or water-based polymeric mixture or system, a whitening agent, a defoamer, a thickener for use in adjusting the final viscosity, and a pH-adjusting component.

A first preferred formulation of a backcoating is presented herewith as Example 1:

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Example 1

- | | | |
|----|---|----------------|
| 1. | DP-101, a water-borne polymeric system consisting of about 34% acrylic/urethane copolymer, 61% water and 5% coalescent solvent, such as M-pyrol | 69.7% to 79.7% |
| 2. | UCD-1060Q, a pre-dispersed whitening agent (titanium dioxide) containing about 72% solids | 21.5% to 23.5% |
| 3. | Balab 3017A, a defoamer | 0.4% to 0.6% |

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|--|--------------|
| 4. CP-15 (50 perc nt in water) acrylic/based thickener to adjust viscosity | 1.5% to 2.5% |
| 5. Ammonia (28 percent aqueous solution) to adjust pH to 8.5 to 10.0 | None to 0.3% |

5 The foregoing mixture is formed by adding the defoamer to the water-borne acrylic/urethane copolymer system with gentle stirring. Thereafter, the whitening agent and the ammonia, if necessary, are added as gentle stirring is continued. The thickener is thereafter added with increasing blade speed and the entire mixture is stirred for about 30 minutes at moderate speed. A preferred mixer for such an operation is manufactured by Meyers Engineering of Bell, California under the trade or model designation "550".

10 DP-101 is a trade designation of Polyvinyl Chemical Industries, Inc. of Wilmington, Massachusetts. While the precise formulation is not known, Polyvinyl Chemical Industries has assigned the trade designation DP-101 *only* to the particular urethane/acrylic copolymer resin utilized in the foregoing backcoat formulation. UCD-1060 is a trade designation of the Universal Color Dispersion Company of Lansing, Illinois, used to identify a dispersion product for water-based systems. Balab 3017-A is also
15 identified by the trade designation "bubble breaker" and is a product of the Organics Division of Witco Chemical Corporation of New York, N.Y. CP-15 is a trade designation of the Rohm and Haas Company and is an acrylic-based thickening agent. M-pyrol is a trade designation of the G. A. F. Corporation used to identify a methylpyrrolidic coalescent solvent. The amount of organic coalescent in the water based systems preferably should not exceed about 10% by formula weight, otherwise the backcoating might
20 permeate the hydrophobic granular matter into the formed cube-corner pattern.

A second formulation for the backcoating mixture is herewith presented as Example 2 and adds a cross-linking agent to improve durability:

Example 2

- | | |
|--|--------------|
| 25 1. DP-101, a water-borne polymeric system consisting of about 34% acrylicurethane copolymer, 61% water, and 5% coalescent solvent such as M-pyrol | 70% to 90% |
| 30 2. UCD-1060Q, a pre-dispersed whitening agent (titanium dioxide) containing about 72% solids | 10% to 20% |
| 3. KYK-W, a defoamer | 12% |
| 35 4. De-ionized water | 5% |
| 5. Ammonia (28 percent aqueous solution) to adjust pH to 8.5 to 9.0 | None to 0.3% |

40 After the foregoing ingredients have been mixed, and immediately prior to application, a quantity of the foregoing mixture is placed in a mixing vessel, and a freshly prepared solution of cross-linking agent is mixed therewith. A preferred cross-linking agent generally is a polyfunctional aziridine, such as CX-100, manufactured by Polyvinyl Chemical Industries, Inc. of Wilmington, Massachusetts. A preferred preparation consists of 15.9 kg (35 lbs). of backcoating mixture combined with 150 grams of CX-100, dissolved in 150 grams of water.

45 BYK-W is a defoamer manufactured by Mallinckrodt of Melville, New York.

In this embodiment, the addition of the cross linking agent enhances the weatherability of the finished laminate by increasing the durability and toughness of the backcoating.

A third formulation for the backcoating material is herewith presented as Example 3:

Example 3

- | | |
|---|----------------|
| 50 1. Emulsion E-1829, a water-borne polymeric acrylic emulsion | 42.1% to 62.1% |
| 2. Water | 2.2% to 12.2% |
| 55 3. Ethylene glycol, an anti-skinning flow improvement agent | 1.5% to 2.5% |
| 4. UCD 1060Q, a pre-dispersed whitening agent (titanium dioxide) | 26.2% to 36.2% |
| 60 5. Syloid 169, silicone dioxide flattening agent to prevent blocking | 3.2% to 5.2% |
| 6. Dimethylamino ethanol pH-adjusting solvent | 0.3% to 0.5% |
| 7. Balab 3017A defoamer | 0.6% to 1.0% |

8. Texanol solvent, a coalescent solvent for improved film formation 1.4% to 1.6%
9. CP-15 (50 percent in water) acrylic-based thickener to adjust viscosity None to 1.6%

5 The foregoing backcoating is prepared by adding the defoamer to the water-borne system with gentle mixing, then adding the water, the anti-skinning agent, the pre-dispersed whitening agent and the amine while continuing gentle mixing. Thereafter, the coalescent solvent is added. Blade speed is then increased and the thickener is added to adjust the viscosity to the desired level and the resulting mixture is then stirred at moderate speed for 30 minutes.

10 Emulsion E-1829 is a trade designation of the Rohm and Haas Company of Philadelphia, Pennsylvania, for an acrylic emulsion vehicle. Syloid is a trade designation of the Davidson Chemical Company, a division of W. R. Grace, of Baltimore, Maryland for a silicon dioxide flattening agent. Texanol is a trade designation of the Eastmont Chemical Products Company of Kingsport, Tennessee used to identify a coalescing agent.

15 Referring now to Fig. 2, a partial sectional view of a schematic portion of embossed thermoplastic web 26 after application of both silica 34 and backcoating 32 is shown. As therein seen, reverse side 30 of thermoplastic web includes a series of valleys, indicated generally at 76. The valleys 76 schematically represent the cube-corner elements found in web 26 when the cube-corner pattern shown in Fig. 1 is embossed onto thermoplastic web 26. When the silica layer 34 is applied, the valleys between adjacent cube-corner elements 76 are filled (except where the screen pattern leaves web 26 exposed) and, in a preferred embodiment of the invention, enough silica 34 is applied to extend a distance of about 2.5 μ m (0.0001 inch) to about 0.076 (0.003 inch) above the embossed surface of thermoplastic web 26, as characterized by dimension A of Fig. 2. In like fashion, the backcoat layer 32 is applied to a thickness B of about 0.05 mm (0.002 inch) to about 0.1 mm (0.004 inch) above the silica layer 34. Where runners or paths 42 are formed, each such runner consists of the backcoat material which extends downward to wet the floor of each valley 76 to a total depth C, as shown in Fig. 2 which, preferably, is about 0.15 (0.006 inch). In a preferred embodiment of the present invention, each such runner is 0.025 mm (0.001 inch) deep and, as characterized by dimension D in Figs. 2 and 6, may be on the order of 0.38 mm (0.015 inch) wide.

In the embodiment herein illustrated, each discrete element of the applied silica pattern is square in shape with the length of each side of the square characterized by dimension E in Figs. 2 and 6. As hereinafter described, the percentage of surface-area available for retroreflection may be adjusted by adjusting the dimensions D and E as shown in Figs. 2 and 6. Where, for example, dimension D is 0.38 (0.015 inch) and dimension E is 5 mm (0.200 inch), the effective surface available for retroreflection is 84 percent. Where dimension D is 0.69 (0.027 inch) and dimension E is 3.5 mm (0.138 inch), approximately 70 percent of the surface of the resulting sheet preserves retroreflective characteristics. With a dimension D of 7.4 mm (0.29 inch) and a dimension E of 2.4 mm (0.096 inch), approximately 55 percent of the total surface of the resulting sheet retains retroreflective properties.

Thus, the degree to which the resulting laminar sheet returns incident light towards its source may be adjusted independent of the actual cube-corner type pattern formed on thermoplastic web 26, in a manner which is much more convenient and efficacious than changing the mold dimensions or characteristics used to produce the embossed cube-corner pattern.

40 Referring again to Figs. 1 and 4, after fourth modified laminate 84 exits drying oven 74, a pressure-sensitive or heat-activated adhesive layer 36 may then be applied by taking the resulting laminate 84 and drawing it past station where a backing or release sheet 38, pre-coated with adhesive 36, may be layered directly onto backcoating 38, resulting in a completed laminate 22 as shown in Fig. 1. Finally, if one is used, the carrier sheet is stripped away, exposing obverse face 28 as the light-receiving surface of the finished laminate 22.

It should be noted that the foregoing examples and preferred embodiments have been presented with respect to a cube-corner embossed pattern having a depth characterized by dimension X in Fig. 2 of 0.1 mm (0.004 inch). It is contemplated that patterns of varying depth and varying dimensions may be utilized, and that the dimensions herein discussed for the depth of silica applied, and the width and depth of the runners thereby formed, may be varied without departing from the spirit and scope of the invention as herein discussed.

55 The finished sheet will have the physical characteristics enabling it to substantially meet specification FP-79 for reflective sheeting, and its reflective properties can easily be varied by utilizing a different screen pattern. Moreover, the whiteness achieved by the existing laminate backcoating substantially enhances the daylight esthetics of the finished material. The heating of the laminate during the drying and curing of the silica, backcoating or adhesive, also may have an effect on the final reflective performance of the laminate, dependent upon the characteristics of the initial tool and the material chosen for the film. It has been determined that for optimum performance, the laminate should not be heated above 82°C (180°F) during these various processing steps for the preferred embodiment disclosed herein.

60 It may also be noted that while the silica pattern herein present is a series of squares turned to present a diamond-like pattern, other cell sizes and shapes are also possible, wherever they appear efficacious for purposes of performance or appearance, and are within the spirit and scope of the invention as herein discussed and claimed.

65 As previously noted, Fig. 7 illustrates a complete embodiment of the present invention. In this

embodiment, a layer 25 of a more weather resistant thermoplastic material than that forming web 26, such as unmodified or UV modified, polymethyl methacrylate, is laminated to the impact modified acrylic forming web 26. In its preferred form, layer 25 will be about 7.6 μm (0.3 mil), and will not exceed 13 μm (0.5 mil) in thickness. It has been found that the provision of this added layer provides additional weathering characteristics needed for certain environments, while, when not exceeding the noted thickness, permits the total laminate to remain sufficiently flexible. Preferred materials in this embodiment may be that sold under the trade designation VO52 or VO44 by the Rohm & Haas Company, or a polyarylate sold under the trade designation Ardel, by Union Carbide. Various techniques may be employed to apply this outer layer to the web before the silica and backcoating is applied. For example, the additional layer of thermoplastic material may be applied by solvent casting or may be co-extruded with the initial film.

A preferred formulation for the outer layer 25 includes use of Korad-D, the trade name of a modified polymethyl methacrylate manufactured by Polymeric Extruded Products, Inc. of Newark, New Jersey. Such material includes U.V. light absorbing substances, and is cross-linked to a flexible, rubber base substance, adding flexibility. In particular, use of Tinuvin 234, a trade mark for a benzotriazol compound manufactured by Geigy, is used as a UV inhibitor. This substance is known chemically as 2,2'-bis(4-methylphenyl)-5,5'-bibenzotriazole. Korad D thermoplastic is described in United States Patent No. 3,562,235, issued on February 9, 1971. When Korad D thermoplastic is used, it may be applied as a 50 μm (2 mil) outer layer during the cube forming process, or it may be co-extruded with the web 26 before such formation, in a layer 25 μm (1 mil) thick, or it may be applied in solution directly to the web 26 in a layer 13 μm (0.5 mil) thick. The particular thickness will depend in part on the total thickness parameters of the finished laminate.

While the foregoing has presented various specific preferred embodiments, it is to be understood that these embodiments have been presented by way of example only.

Claims

1. A method of producing a cube corner type retroreflective laminate sheet construction, the method comprising the steps of:
 - (a) applying to a web of thermoplastic material having a retroreflective cube corner formed pattern devoid of septa on at least a portion of one side, a layer of hydrophobic granular material deposited so as to form a regular and repeating array on the retroreflective pattern;
 - (b) forming, as part of the said array, a plurality of paths on the said one side devoid of the hydrophobic granular material;
 - (c) applying a layer of backcoating material to overlay the hydrophobic granular material and to fill the said path, the particle size of the hydrophobic granular material being such that the area in which it is deposited is substantially impervious to the backcoating material so that the backcoating material is unable to penetrate the granular material and come into immediate contact with the said one side except in the area devoid of the granular material;
 - (d) adhering the backcoating material to encapsulate the hydrophobic granular material between the said one side and the backcoating material; and
 - (e) securing an overlayer of weather-resistant thermoplastic material, containing absorbers or reflectors or radiation in about the ultra-violet range, to that side of the said web opposite to the side on which the cube corner pattern is formed.
2. The method of claim 1, wherein substantially the entire said one side is formed to contain cube corner elements therein and the backcoating adheres to the portions of the cube corner elements devoid of the hydrophobic granular material.
3. The method of claim 1 or 2, wherein the backcoating material initially consists of the following constituents:
 - (a) a water-borne mixture of an acrylic/urethane copolymer in a proportion from about 70 percent to about 90 percent;
 - (b) a whitening agent in a proportion from about 10 percent to about 20 percent;
 - (c) a defoamer in a proportion from about 0.3 percent to about 0.6 percent;
 - (d) a pH adjusting agent in a proportion up to about 0.3 percent; and
 - (e) an aqueous solution of a cross-linking agent in a proportion from about 0.9 percent to about 1.5 percent, by weight, of constituents (a)–(d).
4. The method of claim 3, wherein the cross-linking agent is a polyfunctional aziridine.
5. A flexible retroreflective cube corner type laminate sheet construction produced by the method of claim 1, including a thermoplastic web (26) with a light-receiving and transmitting first side (28) and a second side (30) coextensive with the first side, and a cube corner type retroreflective pattern devoid of septa formed on at least a portion of the second side (30),
 - a layer of hydrophobic granular material (34) covering selected portions of the cube corner retroreflective pattern with remaining portions of the second side (30) devoid of the hydrophobic granular material (34);
 - a layer of backcoating material (32) substantially completely overlaying the hydrophobic granular material (34) and substantially fully contacting the said portions of the second side (30) devoid of the granular material and being fixedly secured thereto, thereby encapsulating the hydrophobic granular

material (34) between the second side (30) and the backcoating layer (32) without penetrating the granular material (34) and coming into immediate contact with the second side (30) except in the area devoid of the granular material; and a lamina (25) of flexible thermoplastic material co-extensiv with and secured to the light-receiving and transmitting first side (28) of the thermoplastic web (26), the said lamina (25) including means for inhibiting radiation in about the ultraviolet range.

6. The construction of claim 5, wherein the said lamina (25) is formed from polymethyl methacrylate in a thickness from about 5 to 10 μm (0.2 mil to 0.4 mil).

7. The construction of claim 5, wherein the said lamina (25) is formed from a rubber-based cross-linked thermoplastic acrylic polymer composition, and the said radiation-inhibiting means is 2 - (2H - benzotriazol - 2 - yl) - 4 - methylphenol.

8. The construction of claim 7, wherein the said lamina (25) is from about 13 to about 51 μm (about 0.5 mil to about 2.0 mil) in thickness.

9. The construction of any of claims 5 to 8, wherein the hydrophobic granular material (34) has a primary particle size of about 18 nm.

10. The construction of claim 9, wherein the hydrophobic granular material (34) has an agglomerated particle size of about 5 μm .

Patentansprüche

1. Verfahren zur Herstellung eines nach dem kubischen Eckentyp retroreflektierenden, laminierten Flachbahnmaterials, dieses Herstellungsverfahren weist die folgenden Schritte auf:

a) Auftragen einer Schicht eines hydrophoben granularen Materials auf eine Bahn aus thermoplastischem Material, die ein retroreflektierendes kubisches Eckenmuster, das auf zumindest einem Teil einer Seite trennwandfrei ist, hat, wobei das granulare Material so aufgetragen wird, daß es eine regelmäßige und sich wiederholende Anordnung auf dem retroreflektierenden Muster bildet;

b) Ausbilden als Teil dieser Anordnung einer Vielzahl von Pfaden auf der einen Seite, auf der sich kein hydrophobes granulares Material befindet;

c) Auftragen einer Schicht aus rückabdeckendem Material zum Überziehen des hydrophoben granularen Materials und Ausfüllen der Pfade, wobei die Partikelgröße des hydrophoben granularen Materials dergestalt ist, daß die Fläche, auf die es aufgetragen ist, im wesentlichen undurchlässig für das rückabdeckende Material ist, so daß dieses das granulare Material nicht durchdringen kann und nicht in unmittelbaren Kontakt mit der einen genannten Seite kommen kann mit Ausnahme der Bereiche, in denen sich kein granulares Material befindet;

d) Verbinden des rückabdeckenden Materials um das hydrophobe granulare Material zwischen der einen genannten Seite und dem rückabdeckenden Material einzukapseln und

e) Befestigen eines Überzugs aus wetterbeständigem, thermoplastischem Material, das Absorber oder Reflektoren für Strahlung im wesentlichen im ultravioletten Bereich enthält, auf diejenige Seite der Bahn, die der Seite gegenüberliegt, auf der das kubische Eckenmuster ausgebildet ist.

2. Verfahren nach Anspruch 1, bei dem im wesentlichen die gesamte genannte eine Seite so ausgebildet wird, daß sie kubische Eckenelemente enthält und die Rückabdeckung an den Portionen der kubischen Eckenelemente haftet, die frei von hydrophobem granularem Material sind.

3. Verfahren nach Anspruch 1 oder 2, bei dem das rückabdeckende Material ursprünglich die folgenden Bestandteile aufweist:

a) Eine aus wässrigem Medium erstellte Mischung eines Acryl-Urethan-Copolymers in einer Proportion von etwa 70% bis zu etwa 90%;

b) Ein Weißmacher in einer Proportion von etwa 10% bis etwa 20%;

c) Ein Entschäumer in einer Proportion von etwa 0,3% bis etwa 0,6%;

d) Ein pH-Einstellmittel in einer Proportion von bis zu etwa 0,3% und

e) Eine wässrige Lösung eines Vernetzungsmittels in einer Proportion von etwa 0,9 bis etwa 1,5 Gewichts % Bestandteilen (a) bis (d).

4. Verfahren nach Anspruch 3, bei dem das Vernetzungsmittel ein polyfunktionales Azitidin ist.

5. Ein flexibles, nach dem kubischen Eckentyp retroreflektierendes, laminiertes Flachbahnmaterial, das nach dem Verfahren gemäß Anspruch 1 hergestellt ist und aufweist: Eine thermoplastische Bahn (26) mit einer lichtaufnehmenden und -weiterleitenden ersten Seite (28) und einer zweiten Seite (30), die gleichgroß wie die erste Seite ist, und ein retroreflektierendes Muster vom kubischen Eckentyp aufweist, das trennwandfrei ist und auf zumindest einen Teil der zweiten Seite (30) ausgebildet ist;

eine Schicht eines hydrophoben granularen Materials (34), das ausgewählte Bereiche des retroreflektierenden Musters in der kubischen Eckenstruktur abdeckt, wobei die verbleibenden Bereiche der zweiten Seite (30) frei von dem hydrophoben granularen Material (34) sind; eine Schicht eines rückabdeckenden Materials (32), die das hydrophobe granulare Material (34) im wesentlichen vollständig überdeckt und im wesentlichen vollständig diejenigen Bereiche der zweiten Seite (30) kontaktiert, die frei von granularem Material sind, und das fest mit diesem verbunden ist, wodurch das hydrophobe granulare Material (34) zwischen der zweiten Seite (30) und der rückabdeckenden Schicht (32) eingeschlossen ist, ohne in das granulare Material (34) einzudringen und ohne in unmittelbaren Kontakt mit der zweiten Seite (30) mit Ausnahme der Bereich zu kommen, die frei von granularem Material sind, und einer dünnen

Schicht (2) eines flexiblen thermoplastischen Materials, das gleich groß wie die lichtaufnehmend und durchlassende erste Seite (28) der thermoplastischen Bahn (26) ist und mit dieser verbunden ist, wobei diese dünne Schicht (25) Mittel für die Blockierung von Strahlung im wesentlichen im UV-Bereich aufweist.

6. Material nach Anspruch 5, bei dem die dünne Schicht (25) aus Polymethyl-Methacrylat in einer Dicke von etwa fünf bis zehn Mikrometer ausgebildet ist.

7. Material nach Anspruch 5, bei dem die dünne Schicht (25) aus einer vernetzten thermoplastischen Acryl-Polymer-Zusammensetzung auf Gummibasis ausgebildet ist, und daß das strahlungshemmende Mittel 2 - (2H - Benzotriazol - 2 - yl) - 4 - Methyl-Phenol ist.

8. Material nach Anspruch 7, bei dem die dünne Schicht (25) eine Dicke von etwa 13 bis etwa 51 Mikrometer hat.

9. Material nach einem der Ansprüche 5 bis 8, bei dem das hydrophobe granulare Material (34) ein primäres Partikelmaß von etwa 18 nm hat.

10. Material nach Anspruch 9, bei dem das hydrophobe granulare Material (34) ein agglomeriertes Partikelmaß von etwa 5 Mikrometern hat.

Revendications

1. Procédé de production d'une structure de feuille stratifiée rétro réfléchissante, du type en coin de cube, ce procédé comprenant les phases suivantes:

(a) l'application à une bande de matière thermoplastique présentant un dessin conformé en coin de cube rétro réfléchissant, dépourvu de cloisons, sur au moins une partie d'une face de cette bande, d'une couche de matière granulaire hydrophobe déposée de manière à former un réseau régulier et répétitif sur le dessin rétro réfléchissant,

(b) la formation, en tant que partie de ce réseau, d'une série de parcours sur la face susdite, ces parcours étant dépourvus de la matière granulaire hydrophobe;

(c) l'application d'une couche de matière dorsale pour recouvrir la matière granulaire hydrophobe et remplir les parcours susdits, la taille des particules de la matière granulaire hydrophobe étant telle que l'aire suivant laquelle cette matière est déposée est pratiquement imperméable à la matière de la couche dorsale, de sorte que cette dernière matière est incapable de pénétrer dans la matière granulaire et d'entrer en contact immédiat avec la face susdite, sauf dans les zones dépourvues de la matière granulaire;

(d) l'adhérence de la matière de la couche dorsale de manière à encapsuler la matière granulaire hydrophobe entre la face susdite et cette matière de couche dorsale; et

(e) la fixation d'un revêtement d'une matière thermoplastique résistante aux intempéries, contenant des absorbeurs ou réflecteurs de rayonnement aux environs de la gamme des ultraviolets, à la face de la bande susdite, qui est opposée à la face sur laquelle est formé le dessin en coin de cube.

2. Procédé suivant la revendication 1, caractérisé en ce que pratiquement la totalité de la première face précitée est formée de manière à présenter des éléments en coin de cube, et en ce que la couche dorsale adhère aux parties des éléments en coin de cube, qui sont dépourvues de la matière granulaire hydrophobe.

3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que la matière de la couche dorsale comprend au départ les constituants suivants:

(a) un mélange flottant d'un copolymère d'acrylique/uréthane en une proportion d'environ 70% à environ 90%;

(b) un agent de blanchiment en une proportion d'environ 10% à environ 20%;

(c) un agent antimousse en une proportion d'environ 0,3% à environ 0,6%;

(d) un agent de réglage du pH en une proportion allant jusqu'à environ 0,3%; et

(e) une solution aqueuse d'un agent de réticulation en une proportion d'environ 0,9% à environ 1,5% en poids par rapport aux constituants (a)-(d).

4. Procédé suivant la revendication 3, caractérisé en ce que l'agent de réticulation est une azitidine polyfonctionnelle.

5. Structure de feuille stratifiée du type en coin de cube, rétro réfléchissante, flexible, préparée par le procédé de la revendication 1, comprenant une nappe thermoplastique (26) présentant une première face (28) de réception et de transmission de la lumière et une seconde face (30) de même étendue que la première, et un dessin rétro réfléchissant du type en coin de cube, sans cloisons, formé sur au moins une partie de la seconde face (30); une couche de matière granulaire hydrophobe (34) recouvrant les parties choisies du dessin rétro réfléchissant en coin de cube, les parties restantes de la seconde face (30) ne comprenant pas de matière granulaire hydrophobe (34); une couche de matière dorsale (32) recouvrant pratiquement totalement la matière granulaire hydrophobe (34) et se trouvant pratiquement en contact total avec les parties de la seconde face (30) qui sont dépourvues de la matière granulaire, en y étant fixée, de manière à encapsuler ainsi la matière granulaire hydrophobe (34) entre la seconde face (30) et la couche dorsale (32), sans que cette couche dorsale pénètre dans la matière granulaire (34) et entre en contact immédiat avec la seconde face (30) sauf dans les zones dépourvues de la matière granulaire; et une feuille (24) de matière thermoplastique flexible, de même étendue que la face (28) de réception et de transmission de la lumière de la bande thermoplastique (26), et fixé à cette face, cette feuille (25) comportant des moyens pour empêcher un rayonnement aux environs de la gamme de l'ultraviolet.

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6. Structure suivant la revendication 5, caractérisée en ce que la feuille susdit (25) est formée de méthacrylate de polyméthyle et est d'une épaisseur d'environ 5 à 10 μm (0,2 à 0,4 millième de pouce).

7. Structure suivant la revendication 5, caractérisée en ce que la feuille susdite (25) est formée d'une composition de polymère acrylique thermoplastique, réticulée, à base de caoutchouc, et en ce que les moyens empêchant le rayonnement sont constitués par du 2 - (2H - benzotriazol - 2 - yl) - 4 - méthylphénol.

8. Structure suivant la revendication 7, caractérisée en ce que la feuille susdite (25) est d'une épaisseur d'environ 13 à environ 51 μm (environ 0,5 à environ 2,0 millièmes de pouce).

9. Structure suivant l'une quelconque des revendications 5 à 8, caractérisée en ce que la matière granulaire hydrophobe (34) comporte une taille de particule primaire d'environ 18 nm.

10. Structure suivant la revendication 9, caractérisée en ce que la matière granulaire hydrophobe (34) a une taille de particules agglomérées d'environ 5 μm .

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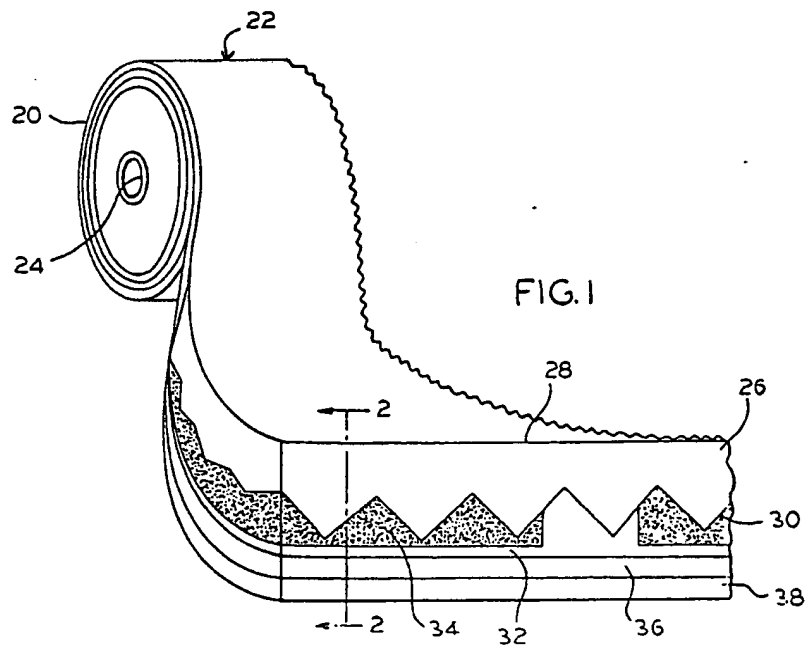
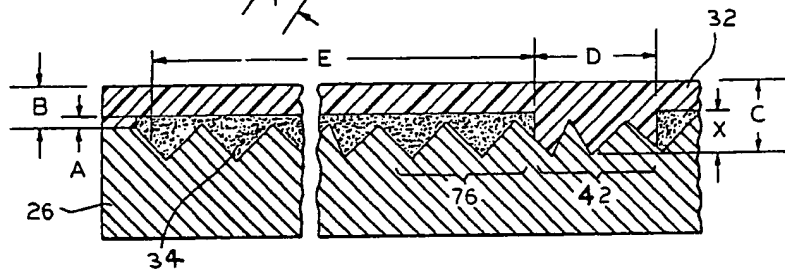
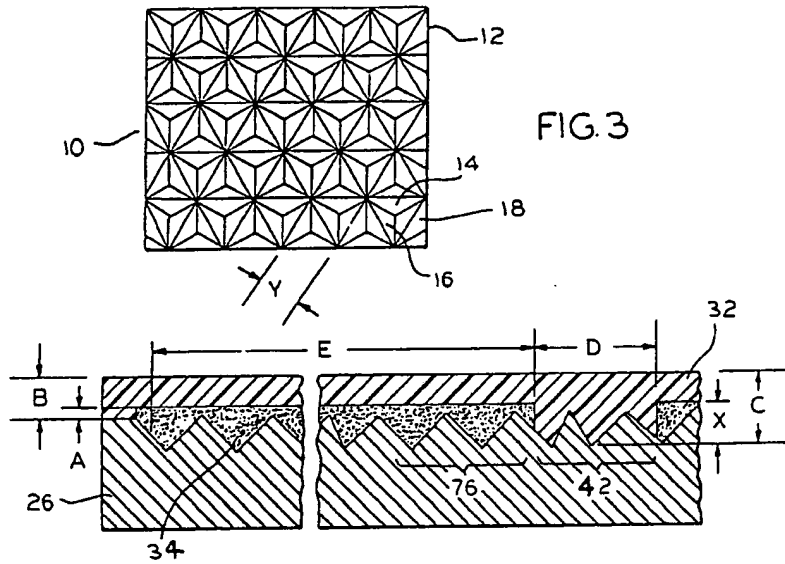
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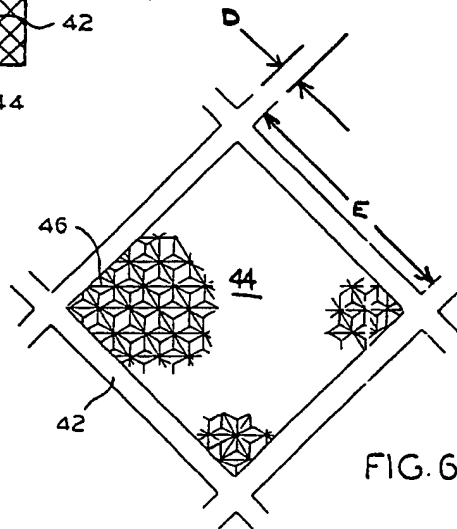
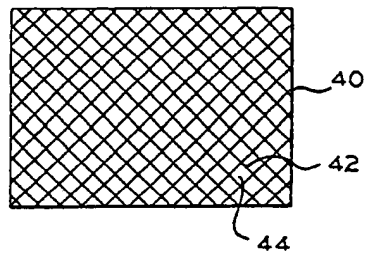
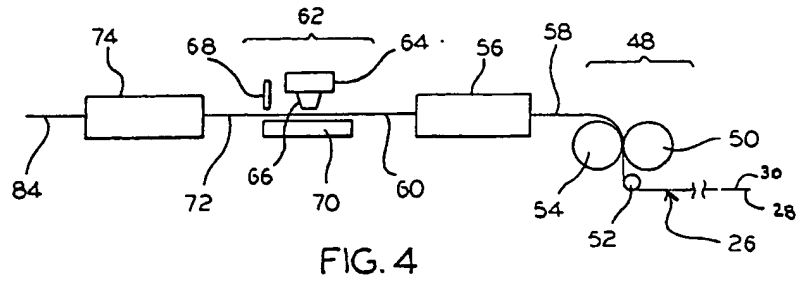
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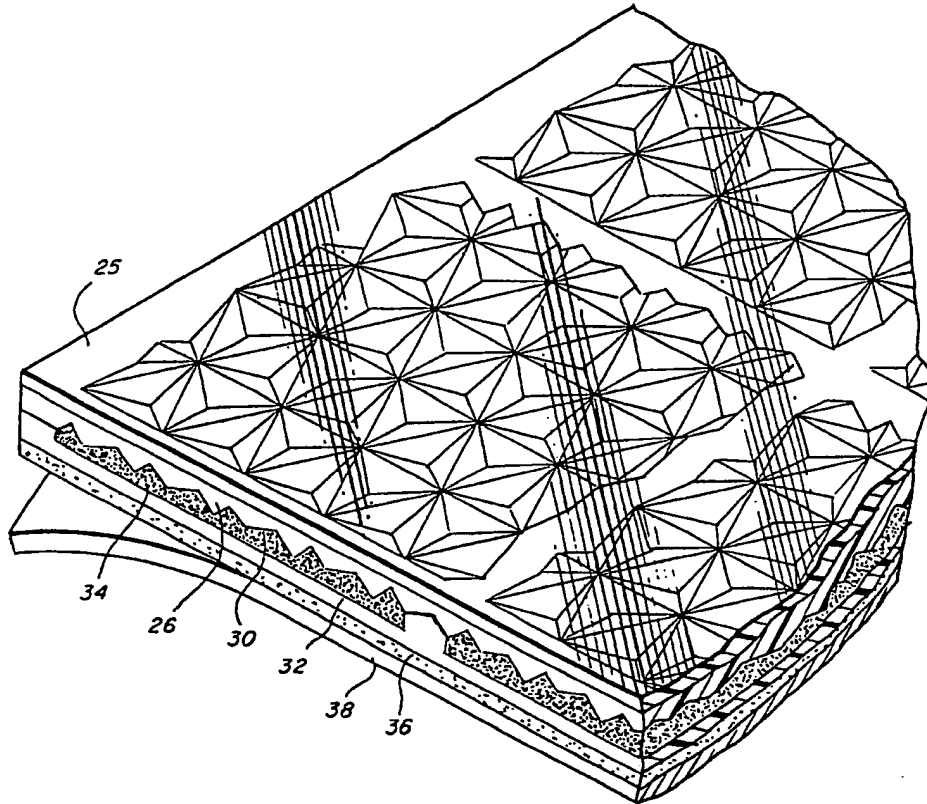


FIG. 7